

THEORETICAL MICROWAVE SPECTRAL CONSTANTS FOR C_3H^+ AND C_4H^+ ¹

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ABSTRACT

Theoretical bond lengths and rotation constants are presented for C_3H^+ and C_4H^+ . Calculations for C_3 are used to assess the accuracy of the former. Recent results for C_2H^+ are also discussed.

Subject headings: molecular processes — transition probabilities

I. INTRODUCTION

A number of linear conjugated carbon chain molecules have been observed in the interstellar gas. It has been suggested that ion molecule chemistry schemes can explain the formation of these compounds. (For a recent article which contains references to earlier work, see, e.g., Schiff and Bohme [1979].) Besides the observed species, these schemes predict that several reactive intermediates—free radicals and molecular ions—might also have detectable abundances. Detection of these would significantly increase our understanding of interstellar chemistry, but this is hampered by lack of laboratory spectral constants. In this regard theoretical estimates can be most useful, as in the case of C_3N and C_4H which have now been identified in radio-astronomical observations (Guélin and Thaddeus 1977; Wilson and Green 1977; Guélin, Green, and Thaddeus 1978). The preceding paper (Green 1980) reports theoretical calculations for several such molecules, C_2N , C_3H , and C_2N^+ . Ion molecule reaction schemes have suggested in particular that C_2N^+ might be quite abundant (Mitchell, Ginsberg, and Kuntz 1978; Hartquist and Dalgarno 1979), and credence has been lent to this by the recent experimental determination of Schiff and Bohme (1979) that this ion is not destroyed by reaction with H_2 . C_3H^+ is isoelectronic with C_2N^+ and is also predicted to be relatively abundant (Mitchell, Ginsberg, and Kuntz 1978). A major purpose of the present work is to present theoretical spectral constants for C_3H^+ . In order to provide some estimate of the reliability of the methods, analogous calculations have been performed for C_3 which is isoelectronic with C_2N^+ and C_3H^+ and for which data are available. Also discussed here are C_2H^+ and C_4H^+ , including new theoretical calculations for the latter.

II. C_3 AND C_3H^+

In order to assess the accuracy of the calculations for the C_3H^+ ion (and the C_2N^+ ion) we first carried out a study of the ground state, $X^1\Sigma^+$ of the isoelectronic C_3 molecule for which experimentally determined bond lengths are available. A second objective here was to compare results of Slater-type (screened exponential) basis functions and Gaussian-type functions; the former were used in the study of C_2N , C_3H , and C_2N^+ reported in the preceding paper, whereas most of our earlier studies (e.g., Wilson and Green 1977) employed the latter. The Slater and Gaussian basis sets were both chosen to be of double zeta size and hence nominally of the same quality. The C_3 molecule was assumed to have $D_{\infty h}$ symmetry. For the Slater basis set the optimized bond length was found to be 2.433 bohr, which is in very good agreement with the experimentally determined value of 2.432 bohr (Hansen, Henderson, and Pearson 1974). The equilibrium bond length obtained with the Gaussian basis set was 2.448 bohr, which is within 0.6% of the experimental value. It would appear that Gaussian and Slater basis functions agree within the 1% uncertainty expected in this type of calculation.

The equilibrium geometry of the C_3H^+ ion was determined by performing self-consistent field molecular orbital calculations using the same two basis sets as employed for C_3 . Equilibrium bond lengths obtained in these calculations are displayed in Table 1 together with those obtained in a previously reported study by Radom *et al.* (1976), which employed a smaller basis set than those used here. The rotation constant, B_e , corresponding to each set of bond lengths is also given.

The bond lengths obtained in the present study using Slater and Gaussian basis sets are within 5 millibohr of each other; the bond lengths obtained by Radom *et al.* differ somewhat more. The rotation constants calculated from these three sets of bond lengths lie within a

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TABLE 1
CALCULATED EQUILIBRIUM GEOMETRIES AND ROTATION
CONSTANTS FOR THE C_3H^+ ION

Basis Set	$R(C_1-C_2)$ (Bohr)	$R(C_2-C_3)$ (Bohr)	$R(C_3-H)$ (Bohr)	B_e (Bohr)
STO-DZ ^a	2.577	2.313	2.051	11.07
GTO-DZ ^a	2.562	2.309	2.050	11.15
STO-3G ^b	2.608	2.292	2.082	11.01

^a Present work. Slater type orbitals, double zeta basis set: STO-DZ; Gaussian type orbitals, double zeta basis set: GTO-DZ.

^b L. Radom *et al.* 1976.

range of only 140 MHz. In view of the calculations for the C_3 molecule, we feel that the calculations on the C_3H^+ ion using the Slater basis set are probably the most reliable. Vibration-rotation interaction will, of course, affect the observed frequencies; however, in previous work on C_3N and C_4H we have neglected these effects and we do likewise here. We estimate that B_0 is 11.1 GHz with an accuracy of about 0.5%. The dipole moment is calculated to be 2.6 debye with an uncertainty of less than 1 debye. Being a closed-shell electronic state, no fine or hyperfine structure will be present.

III. C_2H^+

Because C_2H^+ is known to react rapidly with H_2 , one might assume that it would have a low equilibrium abundance in interstellar clouds. However, detailed calculations based on ion molecule chemistry (Mitchell, Ginsberg, and Kuntz 1978) indicate that in low density clouds—i.e., number densities of 100–1000 cm^{-3} — C_2H^+ has a relatively high abundance. Detection of this species might then provide a good test of these chemistry models, and also a good indicator of H_2 density.

Lathan, Hehre, and Pople (1971) included C_2H^+ in calculations for the structures and energetics of small hydrocarbons. Using minimal Gaussian-type basis set SCF calculations they predicted C_2H^+ to have a linear $^1\Sigma^+$ ground state with $R(CC) = 2.66$ bohr and $R(CH) = 2.10$ bohr. These authors noted that C_2H^+ , like C_2 , should have a low-lying triplet state. (In their SCF calculations the $^3\Pi$ state was actually predicted to be somewhat lower in energy than the $^1\Sigma^+$, but it was argued that, as in C_2 , configuration interaction would preferentially lower the $^1\Sigma^+$ state, making it the ground state.)

As part of a study of C_2H we also performed SCF calculations on this ion several years ago, using a double zeta basis of Slater type orbitals, since this is generally more reliable for predicting bond lengths and rotation constants. As noted by Lathan, Hehre, and Pople (1971) SCF calculations are not likely to predict singlet-triplet splittings accurately, and we considered only the singlet state. It was initially assumed that the electronic configuration was the closed-shell

$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4$, which is obtained by removing the unpaired electron from C_2H . A minimum energy of about -75.569 hartree was obtained near $R(CC) = 2.26$ bohr and $R(CH) = 2.06$ bohr. It was noticed, however, that another $^1\Sigma^+$ configuration was lower in energy (in the SCF approximation) at this geometry, namely the open-shell configuration $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^2$. Using this orbital configuration a minimum energy of -75.6383 hartree was found at $R(CC) = 2.675$ bohr and $R(CH) = 2.07$ bohr. This latter geometry is quite close to that obtained by Lathan, Hehre, and Pople (1971) and, although they do not report the orbital configuration used, we assume that it was the same as ours. Using the equilibrium bond lengths obtained in our calculation gives a rotation constant, $B = 33.3$ GHz. However, this value may not be reliable since the SCF method is not necessarily appropriate when more than a single configuration is needed to describe the wavefunction. We found, in fact, that the closed-shell configuration was lowest (dominant) at small CC distances, and the open-shell configuration was lowest at larger CC distances; a proper description then requires consideration of configuration interaction.

Very recently Montgomery and Dykstra (1979) have reported extensive calculations on C_2H^+ , obtaining “best” bond lengths $R(CC) = 2.272$ bohr and $R(CH) = 2.047$ bohr, giving $B = 44.3$ GHz. These values are considerably different from the small basis SCF values described above. Montgomery and Dykstra used the “self-consistent electron pair” (SCEP) method, which is equivalent, in principle, to a configuration interaction that includes all single and double excitations from some reference configuration; they also approximated the contributions from quadruply excited configurations. Further, they considered several basis sets of which the smallest was double zeta quality. These represent truly immense calculations, and the authors estimate that their rotation constant is accurate to better than $\sim 0.5\%$. We believe, however, that this calculation *might* suffer from a serious problem. The SCEP method as employed by Montgomery and Dykstra was restricted to the case that the wavefunction is well represented by a *single, closed-shell* configuration. These authors therefore assumed that the dominant configuration was $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4$, and it is perhaps not surprising that their bond lengths are rather close to those we obtained for the closed-shell SCF. As noted above, however, this is probably not the proper ground state configuration.

It would appear, therefore, that further calculations for C_2H^+ are needed. Unfortunately, an accurate calculation might be quite difficult since it will have to include interaction among the two low-lying singlet configurations. Further, it is still not clear whether the ground state is $^1\Sigma^+$ or $^3\Pi$ (this point was also noted briefly by Montgomery and Dykstra) and it is notoriously difficult to calculate singlet-triplet splittings accurately (see, e.g., the recent study of the iso-electronic C_2 system by Kirby and Liu [1979]).

IV. C_4H^+

Because a number of longer carbon chain species are observed in space it is of interest to consider higher members in the C_nH^+ sequence. C_4H^+ , like C_2H^+ , suffers from uncertainty about its ground electronic state. It has been inferred from electron spin resonance studies that the ground state of the isoelectronic C_4 molecule is a linear $^3\Sigma^+$ (Graham, Dismuke, and Weltner 1976). Nonetheless, in the preliminary calculations reported here we have considered only the linear $^1\Sigma^+$ state obtained by removing the unpaired electron from C_4H $X^2\Sigma^+$. The equilibrium geometry for this state was obtained from self-consistent field calculations using a Gaussian basis set of double zeta quality. Bond lengths and rotational constants are

presented in Table 2 where they are compared with values from similar calculations for C_4H and HC_4H . The most striking result is the predicted shortening of the central carbon-carbon bond on passing from the neutral to the charged species; it appears that ionization leads to a partial disappearance of bond alternation. The B_e values calculated for C_4H and HC_4H are in remarkable agreement (better than 0.1%) with observed B_0 values. The rotation constant for C_4H^+ is expected to be quite accurate also, unless this species suffers from the same problem as C_2H^+ , i.e., multiple low-lying configurations. Much more extensive calculations than those undertaken here would be required to check this point.

TABLE 2
CALCULATED BOND LENGTHS AND ROTATION CONSTANTS FOR C_4H^+ , C_4H , AND HC_4H ^a

Species	$R(C_1C_2)$	$R(C_2C_3)$	$R(C_3C_4)$	$R(C_4H)$	$B_e(\text{GHz})$
C_4H^+	1.201	1.225	1.204	1.078	5.245
C_4H	1.202	1.387	1.202	1.066	4.753(4.758)
HC_4H	1.200(1.210)	1.386(1.372)	1.200(1.210)	1.066(1.060)	4.387(4.389)

^a Bond lengths in bohr radii (0.52918 Å). Experimental values where known are given in parentheses.

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